

EXHIBIT A

SOFT MECHANOCHEMICAL SYNTHESIS:

A Basis for New Chemical Technologies

by

Evgenii Avvakumov

*Institute of Solid State Chemistry and Mechanochemistry
Siberian Branch of Russian Academy of Sciences
Novosibirsk, Russia*

Mamoru Senna

*Keio University
Yokohama, Japan*

Nina Kosova

*Institute of Solid State Chemistry and Mechanochemistry
Siberian Branch of Russian Academy of Sciences
Novosibirsk, Russia*



KLUWER ACADEMIC PUBLISHERS
Boston / Dordrecht / London

(QD
3/11
A/B
13/14

Contents

Distributors for North, Central and South America:

Kluwer Academic Publishers

101 Philip Drive

Assinippi Park

Norwell, Massachusetts 02061 USA

Telephone (781) 871-6600

Fax (781) 871-6528

E-Mail <kluwer@wkap.com>

Distributors for all other countries:

Kluwer Academic Publishers Group

Distribution Centre

Post Office Box 322

3300 AH Dordrecht, THE NETHERLANDS

Telephone 31 78 6592 392

Fax 31 78 6546 474

E-Mail <orderdept@wkap.nl>

 Electronic Services <<http://www.wkap.nl>>

Library of Congress Cataloging-in-Publication Data

Avvakumov, Evgenii Grigor'evich

Soft mechanochemical synthesis : a basis for new chemical technologies / by Evgenii

Avvakumov, Mamoru Senna, Nina Kosova.

p. cm.

Includes index.

ISBN 0-7923-5431-2

1. Mechanical chemistry. 2. Inorganic compounds--Synthesis. 3. Senna, Mamoru

II. Kosova, Nina III. Title.

QD850.A93 2001

541.3'9—dc21

2001034438

Copyright © 2001 by Kluwer Academic Publishers.

All rights reserved. No part of this publication may be reproduced, stored in a retrieval

system or transmitted in any form or by any means, mechanical, photo-copying, recording,

or otherwise, without the prior written permission of the publisher, Kluwer Academic

Publishers, 101 Philip Drive, Assinippi Park, Norwell, Massachusetts 02061

Printed on acid-free paper.

Printed in the United States of America

PREFACE.....ix

Chapter 1. INTRODUCTION TO SOFT MECHANOCHMISTRY1

Chapter 2. CHEMICAL BONDS, STRUCTURE AND PREPARATION OF

HYDRATED OXIDES.....9

2.1. Chemical bonds in hydrated oxides and their structures.....9

2.2. Properties of hydrated oxides.....20

2.2.1. Acid-base properties.....20

2.2.2. The solubility of hydroxides.....26

2.2.3. Thermal properties.....29

2.3. The preparation of hydroxides.....30

Chapter 3. SOME THEORETICAL ASPECTS OF MECHANOCHMICAL

REACTIONS.....39

3.1. Thermodynamics of acid-base reactions.....39

3.2. The kinetics of mechanochemical reactions.....43

3.3. Energy yield of mechanochemical reactions.....46

3.4. Comparison of soft mechanochemical synthesis with other

methods.....47

3.4.1. Specific features of the preparation of complex oxides from co-precipitated hydroxides.....48

3.4.2. Peculiarities of hydrothermal synthesis.....52

Chapter 4. APPARATUS FOR MECHANOCHMICAL REACTIONS.....59

4.1. Planetary mills.....59

4.2. Vibratory-centrifugal mills.....64

4.3. Ring roll mills.....65

Chapter 4

APPARATUS FOR MECHANOCHEMICAL REACTIONS

23. Ponomarev V.J., Litvin B.N., Belov N.V., Hydrothermal synthesis of calcium hydroaluminates and their X-ray analysis. *Izvestiya AN, Neorgan. Materiali* 1970; 6: 1657-59.

24. Hirano S., Ismail M.G., Sonija S. Crystal growth of sodium titanate bronze compounds under hydrothermal conditions. *Mater. Res. Bull.* 1998; 11: 1013-30.

25. Barsukova M.L., Kuznetsov V.A., Mativovskaya E.K. Crystallization of bivalent metals titanates under hydrothermal conditions. *Kristallografiya* 1972; 17: 1288-70.

26. Ilukhin V.V., Kuznetsov V.A., Lobachev A.N., Bakschyov V.C. *Calcium Hydrosilicates*. Moskva: Nauka, 1979.

27. Komiljenovic M.M., Radatovic A., Zivanovic B.M. et al. An investigation of solid- and liquid-state reactions in CaO-SiO_2 system. *Science of Sintering* 1994; 26: 185-93.

28. Boldyrev V.V., Khabibullin A.Kh., Kosova N.V., Avvakumov E.G. Hydrothermal reactions under mechanochemical treatment. *J. Mater. Synthesis Proc.* 1996; 4: 377-81.

29. Kosova N.V., Khabibullin A.Kh., Boldyrev V.V. Hydrothermal reactions under mechanochemical treating. *Solid State Ionics* 1997; 101-103: 53-58.

Mechanochemical reactions are carried out by means of mechanical activation in high energetic apparatus. Grinding devices with high load rates are used for this purpose, such as planetary, vibratory centrifugal, shock-reflective and ring roll mills, attritors, etc.

4.1. Planetary mills

Relatively new and promising high energetic planetary and differential centrifugal mills were developed by Bushuev, Golosov and other authors [1-6]. High rate of grinding and activation in these mills is provided by centrifugal forces arising at the rotation of each jar around its own axis and their common axis. These centrifugal forces exceed the gravity force by a factor of several tens, thus, providing the energy of these mills by 2-3 orders of magnitude higher than that of common ball mills. Powder dispersion achieved in a centrifugal mill after 2 min treatment is the same as that achieved in usual ball mill after the treatment for 10-12 h. The most of results reported in the present book were obtained mainly with planetary mills of periodic action that were improved and adapted to carry out mechanochemical reactions in a closed system with external cooling.

In new laboratory planetary mills, the jars rotate due to frictional clutch with the cylindrical housing of the mill. A scheme and the design of the apparatus are shown in Fig. 4.1 [5]. The apparatus consists of the housing 1, carrier 2, jars 3, guiding rim 4, sheave 5, channels in the center and at the periphery of the carrier for cooling water. The diameter of the jars is 70 mm, the working volume is 150 cm³, ball mass is 200 g, the mass of the substance under treatment is 10 g.

The device operates as follows. At first, water is admitted from water pipeline through the tube 6 and channels 7 into the pockets 8. When the motor (not shown in the scheme) is switched on, the carrier starts to rotate; the rings that are fixed on it make jars rotate. The surfaces of jars and rings are separated from each other by water layer, like in hydrostatic bearings: the jars operate as a spindle while the ring acts as hydrostatic bearing. Under the action of centrifugal forces, the jars are pressed to the

guiding rim 4 and due to frictional clutch with its surface rotate around their axis. Thus, the jars take part in two kinds of rotation: around their common and own axes. This technical solution excludes the necessity to use bearings in the most loaded part of the mill (the drive of jars) and increases operational lifetime of the apparatus. Intensive cooling of the jars by water decreases the contamination of the product with the material of grinding

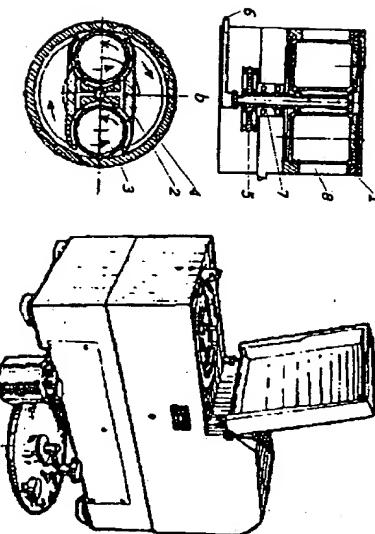


Figure 4.1. The scheme of operation and design of the AGO-2 planetary mill [5].
a - view from side, b - view from above.

bodies as well as increases the degree of product activation since the annealing of defects is excluded.

In order to characterize the operational regime of the planetary mill, k and m parameters were introduced. $k = \omega_2/\omega_1$ (here ω_2 is a frequency of rotation around the planetary axis and ω_1 is a frequency of rotation around the common axis), and $m=R_2/R_1$ (R_1 and R_2 are the radii of common and planetary rotation).

The value of k can be either positive or negative. This depends on the direction of vectors of relative and planetary rotation of the jars. When these directions are the same, k is positive, but if the vectors are directed opposite to each other, k is negative. The most efficient regimes of the planetary mill are within the range when $k = -1$.

According to [4], theoretical power of the planetary mill can be calculated according to the equation:

$$W_{\text{plan.}} = (W_{\text{ball}} \cdot 4\pi^2 R_1 \omega^2 / 981) \cdot n_1 / n_2 \quad (4.1)$$

here W_{ball} is equal to the power of the ball mill:

$$W_{\text{ball}} = 6.1 P \sqrt{D}, \quad (4.2)$$

P is a mass of balls, kg; D is a jar diameter, m; ω is a frequency of rotation (of the rotor), s^{-1} ; n_1 is a critical rotation frequency of the planetary mill which is equal to

$$n_1 = 0.8 \sqrt{R_1/R_2}; \quad (4.3)$$

n_2 - critical number of revolution in ball mill which is equal to

$$n_2 = 32 \sqrt{D}. \quad (4.4)$$

Energy parameters of laboratory planetary mill were determined experimentally in [7,8]. The power was determined by means of calorimetry. Water flow temperature was measured at the inlet (T_1) and at the outlet (T_2); the calculation was performed according to the equation

$$Q = mc(T_2 - T_1), \quad (4.5)$$

where Q is the power scattered by a jar as a heat, m is a mass, C is a heat capacity of water.

A blank experiment was carried out with balls being replaced by immobile plate of equal mass. This contribution was subtracted from the total energy consumed. The results are shown in Table 4.1.

Table 4.1. The power of the laboratory planetary mill determined experimentally (balls mass 100 g, the substance to be treated: 10 g) [8].

The frequency of total rotation, rpm	Power, W	
	Ball diameter: 5 mm	Ball diameter: 9 mm
602	191	104
858	271	204
996	602	389

As one can see, energy consumption by the present mill is equal to

$$10.60 \text{ W/g.}$$

Besides total energy consumption for mechanochemical reactions, the level of local parameters of temperature and pressure arising in the mill is also important. It is very difficult to measure these parameters directly during activation. Therefore, an indirect method based on P and T determination of phase transitions under mechanical activation of the

substances with known P-T phase diagrams was used [9]. The results are shown in Table 4.2.

Table 4.2. Phase transitions observed in a planetary mill (the frequency of total rotation: 836 rpm) [9].

Phase transition	P, GPa	T, K	Result
$\beta\text{-PbO}_2 \rightarrow \alpha\text{-PbO}_2$	1.3	0 - 673	+
$\text{H-Nb}_2\text{O}_5 \rightarrow \text{T-Nb}_2\text{O}_5$	1.1 - 1.5	400 - 500	+
$\text{Pb}_3\text{O}_4 \rightarrow \text{PbO} + \text{Pb}_2\text{O}_3$	1.8 - 3.0	473 - 673	+
$\text{T-Nb}_2\text{O}_5 \rightarrow \text{B-Nb}_2\text{O}_3$	3.0	773	-
$\text{TiO}_2 \rightarrow \text{TiO}_2$ (high pressure)	4.0	-	-

It follows that in the mill, local temperatures arise up to 600-800 K and pressure - within 2-3 GPa. Other authors confirmed these data

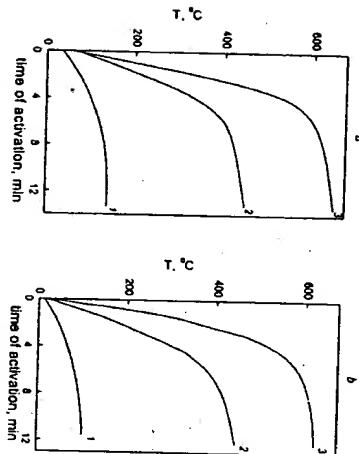


Figure 4.2. Changes of the temperature of balls in the planetary mill, depending on activation time, rotation frequency, and ball size [8].
 a - rotation frequency, s^{-1} : 1 - 10.2, 2 - 14.3, 3 - 16.5,
 b - ball diameter, mm: 1 - 3.2 - 5.3 - 9.

experimentally. For example, in [8] the ball temperature was determined from the calorimetric data. The authors calculated ball temperature

according to heat balance equation having determined a total heat of the jar and balls. The data for different rotation frequencies and ball diameters are shown in Fig. 4.2. With increasing the ball size and the frequency of total rotation, temperature increases and reaches a level of about 873 K. High temperature of large balls is due to the generation of heat at inelastic deformation of balls during their collisions with a wall and due to worse heat exchange conditions in this case.

In [10], a comparison of the power of different mills at optimal regimes of their operation was carried out. Some of the results are shown in Table 4.3.

Table 4.3. Comparison on the power of different mechanochemical activators [10].

Mill type	Frequency, s^{-1}	Ball diameter, mm	Ball mass, g	Mass of powder, g	Power per 1 g of powder, W/g
Planetary, A GO-2	11.4	9	100	4	10
Planetary, Pulverizette 7	4	9	53	2	0.3
Vibratory, M-35	50	9	107	10	1.2
SPC-8000	-	6	307	2	9

As one can see, among the mills used for mechanochemical investigations, A GO-2 planetary mill exhibits better characteristics.

A middle-scale mill A GO-3 was constructed for operation in periodic regime [6]. A principle of hydrostatic bearing in A GO-3 mill is the same as in A GO-2 mill. The jars rotate around the common and own axes due to frictional engagement with the surface of the cylindrical guide surface. The volume of a jar (their number in the carrier being three) is 2 dm^3 . Total ball mass is 2 kg; the mass of substance under treatment is 300 g per one jar. The amount of product that can be prepared within one working day is equal to 7-10 kg.

4.2. Vibratory-centrifugal mills

Vibratory-centrifugal mills, developed by Denisov with coauthors [11] and marked as 5G, 10G, 30G, 50G, could be successfully used for continuous operation to carry out mechanochemical syntheses under industrial conditions.

Fig. 4.3 shows the design of this vibratory mill. It is constructed with horizontal position of the milling jars with the tube form. They are rigidly fixed on carriers and move together with them along the circle trajectory in a plane perpendicular to the axes of jars; the jars do not rotate along their own axes; their orientation in the vertical plane remains unchanged.

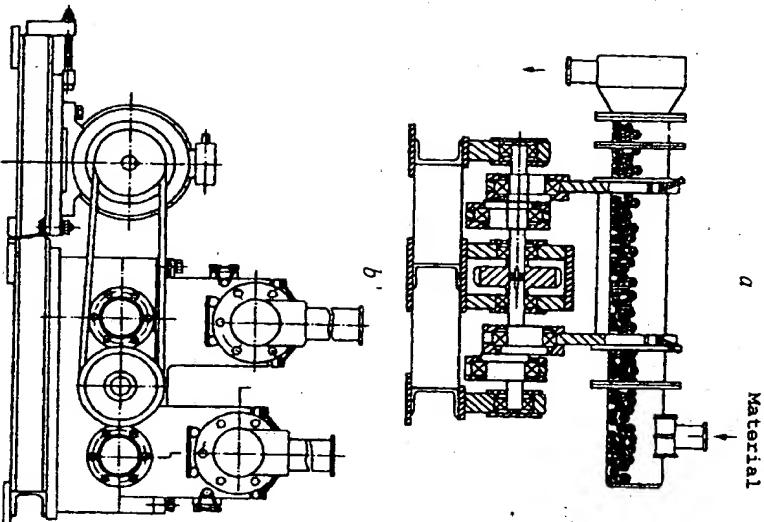


Figure 4.3. The scheme of vibratory-centrifugal mill of continuous action [11].
a - view from side, b - end view.

As a result of this motion, the material under treatment and milling bodies inside the milling jar are subjected to the overall action of centrifugal,

gravity and Coriolis forces. This creates inside the jar the conditions providing the material to be subjected to intensive action of vibration shock, attrition and crushing loads that results in grinding and activation of the treated material.

The main working elements of the mill are eccentric crankshafts with the pairs of eccentrics on them. The eccentrics in a pair are counter to each other, i.e., their eccentricities lie strictly in one plane and are opposite directed. At synchronous rotation of crankshafts, grinding blocks connected to opposed eccentrics move around circles, their motions being shifted in phase by 180° with respect to each other. At every moment they are in static equilibrium; thus, the mill does not require balancing adjustment, except the following: the weight of milling bodies in each jar as well as the weight of treated material should be equal per unit time.

The rotation is passed to the drive shaft of the motor through a V-belt transmission. The drive shaft rotates crankshafts synchronously and transmits the motion to milling blocks. The productivity of the mill depends on the size of jars, the frequency of shaft rotation, rate of material admittance through the jars, etc. Centrifugal mills providing the productivity of 5+50 kg per hour have been constructed.

4.3. Ring roll mills

The ring roll mills MICRO, constructed and produced by Nara Machinery Co., LTD, Tokyo appeared to be high-effective for soft mechanochemical reactions to occur. The grinding of the particles is realized by compression and shearing forces generated by the rotating grinding rings. The scheme of the mill and the principles of its work are presented in Fig. 4.4.

The main body of the MICRO consists of a casing, revolving main shaft in the casing and several sub-shafts interlocked with the rotation of the main shaft. Each sub-shaft has a number of rings shaped grinding media. The size of the ring as a grinding body is different depending upon models. The outside diameters are of 25+45 mm and thickness of several mm.

The equipment is designed in such a way that each ring moves freely, allowing a small space between the outside diameter of the sub-shaft and the inner diameter of ring. The ring moves radial as much as the space allows by the centrifugal force created by the rotating main shaft and keeps turning by being pressed toward the inside wall of the casing. At this moment, the ring rotates itself around the sub-shaft by the friction force with wall surface. This means that while the ring revolves in the casing, the latter also rotates.

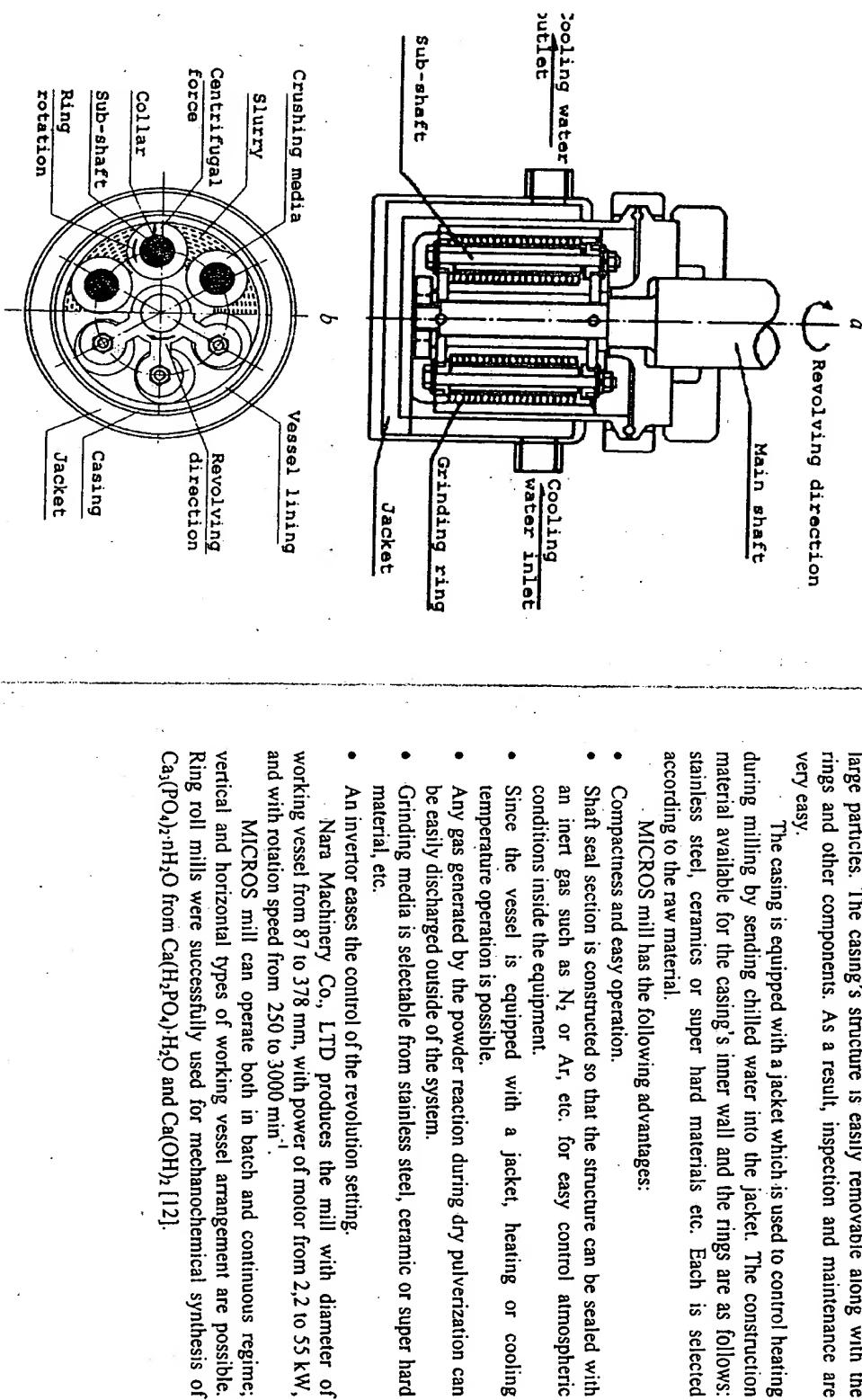


Figure 4.4. The scheme of the operation of MICROOS ring roll mill [12].
 a - view from side, b - view from above.

The particles are held between the revolving ring and the wall surface, and are subjected to compressing force created by the centrifugal force of the ring and the friction created by the rotation ring. This process generates pulverization and dispersion of the particles.

Since the rings are allowed to move freely, an independent crushing effect is given to the particles even when the fed material contains small and

large particles. The casing's structure is easily removable along with the rings and other components. As a result, inspection and maintenance are very easy.

The casing is equipped with a jacket which is used to control heating during milling by sending chilled water into the jacket. The construction material available for the casing's inner wall and the rings are as follows: stainless steel, ceramics or super hard materials etc. Each is selected according to the raw material.

MICROS mill has the following advantages:

- Compactness and easy operation.
- Shaft seal section is constructed so that the structure can be sealed with an inert gas such as N₂ or Ar, etc. for easy control atmospheric conditions inside the equipment.
- Since the vessel is equipped with a jacket, heating or cooling temperature operation is possible.
- Any gas generated by the powder reaction during dry pulverization can be easily discharged outside of the system.
- Grinding media is selectable from stainless steel, ceramic or super hard material, etc.
- An inverter eases the control of the revolution setting.

Nara Machinery Co., LTD produces the mill with diameter of working vessel from 87 to 378 mm, with power of motor from 2,2 to 55 kW, and with rotation speed from 250 to 3000 min⁻¹.

MICROS mill can operate both in batch and continuous regime; vertical and horizontal types of working vessel arrangement are possible. Ring roll mills were successfully used for mechanochemical synthesis of Ca₃(PO₄)₂·nH₂O from Ca(H₂PO₄)₂·H₂O and Ca(OH)₂ [12].

References

1. Bushuev L.P. On design and application of planetary mills. *Izvestiya Vusov, Gomii Zhurnal* 1960; 2: 17-20.
2. Bushuev L.P. Multiregime planetary mill. *Izvestiya Vusov, Mashinostroenie* 1964; 10: 17-22.
3. Patent RU №101874, 1955. Centrifugal planetary mill. Golosov S.I.
4. Golosov S.I., Molchanov V.I. *Physico-chemical changes of minerals during fine grinding*. Novosibirsk: Institute of Geology and Geophysica, 1966.
5. Patent RU № 975068, 1982. Planetary mill. Avvakumov E.G., Potkin A.R., Samarin O.I.
6. Patent RU № 158203, 1993. Planetary mill. Avvakumov E.G., Potkin A.R., Bereznyak V.M.
7. Avvakumov E.G. *Mechanical Methods of Activation of Chemical Processes*. Novosibirsk: Nauka, 1986.
8. Gerasimov K.B., Gusev A.A., Kolpakov V.V., Ivanov E.Yu. Measuring of background temperature of mechanical alloying in planetary mill. *Sibirskii Khim. Zhurnal* 1991; 3: 140-45.
9. Avvakumov E.G. Mechanical activation of reactions between solid inorganic substances. Proc. V Symposium TATARAMAN, Bratislava, 1988; 2: 21-26.
10. Borunova A.B., Zhermovenkova Yu.V., Streletska A.N., Portnoy V.K. Determination of energy intensity of mechanochemical reactors of different types. Book of Abstracts of INCOME-3, Prague, 4-8 September, 2000.
11. Patent RU № 2001680, 1993. Vibro-centrifugal mill. Denisov M.G., Denisov G.A., Novikov G.N.
12. Liao J., Ono K., Kanayama G., Isobe T., Senna M. Preparation of tricalcium phosphate by applying grinding technique and choosing hydroxycontaining initial materials. *Chemistry for Sustainable Development* 1998; 6: 233-36.



of hydrogen bonds, which are the precursors for preparation of final products by the following thermal treatment:

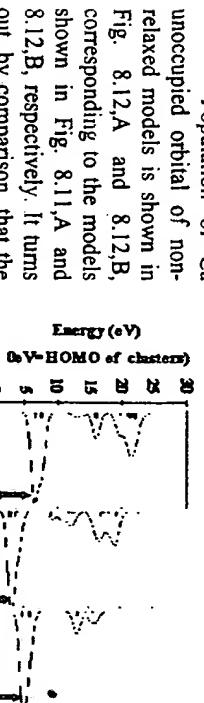


Figure 8.12. Orbital population of calcium unoccupied orbitals in cluster models in Fig. 4(c). (A) No vacancy (without surface relaxation). (B) One OH vacancy (without surface relaxation). (C) One OH vacancy (with surface relaxation).

Figure 8.12. Orbital population of calcium unoccupied Ca orbital, pointed by arrows, lowers against the HOMO of the cluster by removing an OH group. This is in accordance with the previous result on CaO surface, which disregards surface relaxation [21]. However, for the model accounting for the surface relaxation (Fig. 8.11,C), the energy of the unoccupied Ca orbital hardly lowers, in spite of forming of low coordinated Ca (Fig. 8.12,C). (A) No vacancy (without surface relaxation), (B) One OH vacancy (without surface relaxation), (C) One OH vacancy (with surface relaxation).

themselves significantly. A large deviation of the resulting atomic positions from that in the ideal crystal lowers the symmetry of the crystalline lattices, and accordingly, makes a Madelung potential more asymmetric. This, in turn, forces a decrease of all the energy levels of Ca atoms to minimize the total potential energy of the reaction system. The energy difference between Ca_{out} (or Ca_{in}) and O_{p} decreases, while the difference between Ca_{in} (or Ca_{p}) and O_{p} increases. These changes intensify the bonding overlapping between Ca_{out} and O_{p} toward apparent bonding molecular orbitals, while decrease the antibonding interaction between Ca_{in} and O_{p} . The increasing covalent nature, thus established, stabilizes a Ca-O wing of a Ca-O-Si bridging bond with respect to the other wing, O-Si, and finally, stabilizes the bridging bond as a whole.

8.3. Role of water in soft mechanochemical reactions

Neutralization in aqueous solutions is characterized by low activation energy and occurs very rapidly. On contrary, in the case of acid-base interaction between solids, it is multistage process and can be accompanied by the formation of stable compounds with the participation

The possibility of mechanochemical reactions to occur via hydrothermal mechanism was demonstrated in [32] for the synthesis of calcium hydrosilicates. Optimal water content values (humidity) of solid mixtures of correspondent hydrates were estimated for the achievement of local hydrothermal conditions (elevated temperature and pressure) in mechanochemical activators. It was shown experimentally that the main factor determining the kinetics and composition of the products was the molar fraction of the components, the same as for hydrothermal reactions, while the effect of temperature and pressure was much weaker.

While studying the mechanism of mechanochemical synthesis of magnesium silicate, it was shown that the components are dissolved in the liquid phase and interact with each other [33]. At first, the precipitation of hydrosilicates from the solution in fine disperse and X-ray amorphous state occurs. Then the growth of larger crystals takes place. Therefore, the products are not detected directly after mechanical activation; some exposure is necessary for them to be crystallized.

It is known that the contact of two solids results in the appearance of adhesion strength due to the interaction between surface atoms. It has been stated that the interaction forces are changed with the distance between the surfaces of the condensed solids as $1/r^3$ [34,35]. Specific attraction forces are equal to 0.15 MPa at a distance of about 10 nm, 30 MPa at 3 nm, and reach 110 MPa at 1 nm. This means that at a distance of the order of atom size, van der Waals forces become very large, that helps redistribution of electrons to form a new chemical bond.

CaO-4TiO₂.6H₂O [29] while in activated La(OH)₃+TiO₂.aq mixture the formation of La₂[TiO₂(OH)₂].nH₂O is observed [30]. The mentioned compounds are decomposed at 600-800°C with the formation of anhydrous complex oxides.

The possibility of mechanochemical reactions to occur via hydrothermal mechanism was demonstrated in [32] for the synthesis of calcium hydrosilicates. Optimal water content values (humidity) of solid mixtures of correspondent hydrates were estimated for the achievement of local hydrothermal conditions (elevated temperature and pressure) in mechanochemical activators. It was shown experimentally that the main factor determining the kinetics and composition of the products was the molar fraction of the components, the same as for hydrothermal reactions, while the effect of temperature and pressure was much weaker.

The possibility of mechanochemical reactions to occur via hydrothermal mechanism was demonstrated in [32] for the synthesis of calcium hydrosilicates. Optimal water content values (humidity) of solid mixtures of correspondent hydrates were estimated for the achievement of local hydrothermal conditions (elevated temperature and pressure) in mechanochemical activators. It was shown experimentally that the main factor determining the kinetics and composition of the products was the molar fraction of the components, the same as for hydrothermal reactions, while the effect of temperature and pressure was much weaker.

It is known that the contact of two solids results in the appearance of adhesion strength due to the interaction between surface atoms. It has been stated that the interaction forces are changed with the distance between the surfaces of the condensed solids as $1/r^3$ [34,35]. Specific attraction forces are equal to 0.15 MPa at a distance of about 10 nm, 30 MPa at 3 nm, and reach 110 MPa at 1 nm. This means that at a distance of the order of atom size, van der Waals forces become very large, that helps redistribution of electrons to form a new chemical bond.

The strength of secondary formations (agglomerates), in which mechanochemical reaction occurs under mechanical action, are substantially affected by the medium used at activation. In high vacuum, the particle surface gets free from the adsorbed molecules, and the efficiency of the interaction between surface atoms increases. In the presence of liquids, especially polar ones, such as water and alcohol, molecular-dense aggregates decompose to give primary particles. That is why mechanical activation in the presence of these liquids yields finely dispersed products. The efficiency of chemical interactions between components in these systems is insignificant due to the absence of good contacts.

However, if the dispersion of a mixture of components is high and water concentration is small, so that it forms 1-3 molecular layers on the surface of solid particles, quite different phenomenon is observed. Water acts as a binding agent and improves the strength of the agglomerates [36]. The nature of intergrain contacts in these systems is determined by hydrogen and donor-acceptor bonds of water molecules with surface atoms or surface groups (e.g., OH groups) of the disperse phase.

As a rule, the surface of the disperse phase is hydroxylated (=Si-OH, =Al-OH, etc.); surface atoms possess valence d-orbitals. Therefore, the formation of adsorption water layers occurs not only via the formation of hydrogen bonds but also due to donor-acceptor bonds. It is this phenomenon that forms the grounds of wetting of solids with water.

Due to the structuring of water layer and the action of surface fields on water layers, hydrogen bonds become stronger; their energy becomes higher by a factor of 2-2.5 than that of hydrogen bonds in the water bulk, water itself exhibiting others properties ($\rho=1.2 \text{ g/cm}^3$, dielectric permeability ≈ 5) [35].

In the presence of electrolyte solutions, hydrated cations and anions participate in the formation of contacts and determine their strength. The addition of electrolytes can either increase the structuring of water layers or, vice versa, weaken this process (positive and negative hydration). Some electrolytes strengthen water structure, the others weaken it. In the first case, the viscosity of water increases; in the second case it decreases. The first group consists of polyvalent electrolytes and the electrolytes, such as halides of alkaline elements, while the second group - of some electrolytes, such as KI.

An increase of the contact strength with the decrease of water layering is confirmed experimentally. For example, it was stated that the strength of raw material formed from wetted bentonite is determined by the equation:

$$\sigma_{\text{compress}} = a n^b, \quad (8.4)$$

where a, b are constants, n is a number of water monolayers calculated on the basis of the given specific surface and water amount [35].

When studying the effect of the amount of water on the efficiency of interaction in the mixture of anhydrous oxides (CaO and TiO_2) and hydrated ones ($\text{Ca}(\text{OH})_2$ and H_2TiO_3), an extremal dependence of the degree of components binding into product versus water content was found (Fig. 8.13) [37,38]. The maximum observed in this dependence can be explained from the viewpoint of the mentioned notions. At low water content, it makes the agglomerates of anhydrous oxides stronger, that helps chemical interaction to occur. At increased amount of water, the agglomerates are destroyed and chemical interaction decreases.

The presence of a maximum in this dependence allows to identify a new type of distinctive interactions, differing from those in the mixtures of solids and in aqueous solutions, namely, in the type of solid state mechanochemical reactions occurring at low concentration of water.

8.4. Mechanochemical ligand exchange as a new concept of solid state synthesis

When mechanical stress is exerted on molecular crystalline solids of coordination compounds, not only crystalline lattice but also the constituent molecules are subjected to distortion. The type and extent of distortion of each molecule is inevitably different due to the anisotropic nature of mechanical stressing. This, in turn, causes disproportionation of their ligand fields to decrease their symmetry.

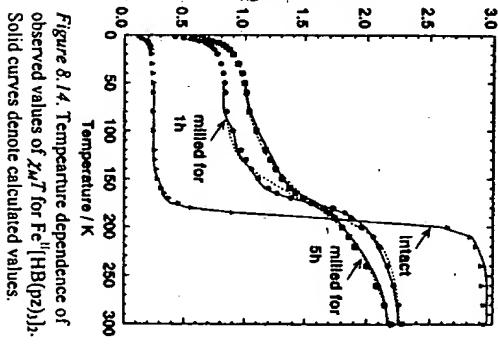


Figure 8.13. The degree of interaction of calcium oxide with titanium oxides as a function of water content:
1 - $\text{CaO} + \text{TiO}_2$ (anatase);
2 - $\text{Ca}(\text{OH})_2 + \text{H}_2\text{TiO}_3$.

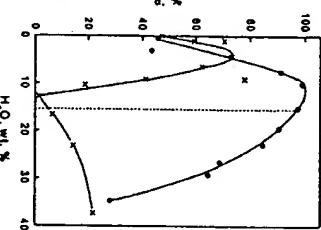


Figure 8.14. Temperature dependence of observed values of $\chi\mu T$ for $\text{Fe}^{\text{II}}\text{HB}(\text{pz})_2$. Solid curves denote calculated values.

Mechanochemistry and mechanical activation of solids

V.V. Boldyrev

*Institute of Solid State Chemistry, Siberian Branch of the Academy of Sciences of Russia,
Derzhavina 18, 630091 Novosibirsk 91, Russia*

The paper reviews investigations on mechanochemistry and mechanical activation of solids and discusses the most urgent problems which concern this field.

1. Introduction

The mechanical treatment of solids is one of the most common and widely used operations with which man has been concerned from the very beginnings of the history of civilization. Indeed, the volume of solids subjected to chemical treatment is very large. Thus, for instance, every year over a milliard tons of solids is subjected to comminution, grinding involving a large electric energy consumption. Many tons of high-quality alloys are expended for the manufacture of comminution apparatus [1]. The same may be also said about other kinds of mechanical treatment.

Until recently, it has been customary to assume that this field of science belongs to the "diocese" of physics. As to the chemical consequences of mechanical treatment, here everything seemed to be clear from the very beginning, proceeding from the so-called "knowledge of life" or "everybody's experience".

Thus, until very recently, it has been universally recognized that the cause of chemical reactions occurring during mechanical treatment of solids is heat evolution after the treatment and, arguing for this idea, one could refer to the work of an ordinary lighter or a match.

Analogously, a change in the reactivity of solids due to mechanical treatment was considered to be the result of increase in the specific surface of the solid upon treatment. Indeed, in support of this idea,

everyone could claim that before salting the soup the salt should be pounded.

However, a more detailed investigation of the processes occurring during mechanical treatment of solids has shown that these "universally recognized" truths are far from being always right. The chemical processes occurring during mechanical action on solids turned out to be more specific and versatile than they have been considered so far. This has stimulated the development of investigation in the field of mechanochemistry, a young but rapidly developing area of chemical science. In my lecture, I shall try to show some aspects of this science using as examples experimental data obtained at the Institute of Solid State Chemistry.

2. Specifics of mechanochemical reactions

As an example, consider the simplest reaction initiated mechanochemically – a reaction of decomposition. Based on the very general concepts of the mechanism of chemical processes in solids, a decomposition reaction may be presented as a certain sequence of stages including the formation of an excited state, the rupture of chemical bonds, and the removal of the reaction products or system relaxation to the initial state [2,3].

In accordance with this, all the decomposition processes may be conventionally divided into two groups. The first of these includes those processes which are controlled by the excitation stage. A ther-

mal decomposition reaction is a good example of this group. The second group comprises the processes in which the rate limiting stage is the stage which involves the subsequent steps of the process (photolysis, radiolysis). A very simple test has been proposed for estimating, in a first approximation, to which of these groups the process we are interested in belongs. To do this, one should compare the stability series of salts of the same type. Thus, for instance, it is well known that in the series of alkaline nitrates and bromates the thermal stability increases in going from lithium to caesium. As is well known, in the series of these salts, the radiational-chemical and photochemical stability changes in reverse order [3]. If now a comparison is made of the mechanochemical stability in the series of these salts, it can be concluded to which of the processes the mechanical decomposition is similar, either to thermal decomposition or to photolysis, or radiolysis. This has been done in refs. [4,5]. The results of such a comparison have shown that, despite the mechanochemical decomposition of nitrates and bromates conducted under different conditions and by different methods (in one case the salts are treated in a planetary mill and in the other they are exposed to a shock wave), the series of mechanochemical stability of nitrates and bromates resembles largely the series of photolysis and radiolysis rather than those of thermal stability. Besides, it turned out that the products formed in the thermal and mechanochemical decomposition of the same salts are different [5].

Similar results have been obtained in studies of chemical processes occurring at the tip of a moving crack. These studies are of particular interest due to the very specific conditions which arise in the crystal nearby the tip of a moving crack.

On the one hand, a very large concentration of stress field occurs here, on the other hand, this particular site moves over the crystal with a very high velocity. To study the chemical processes occurring at the tip of a moving crack, Fox and Loria-Rutz [6] have used a set-up which allows a crystal to be cleaved directly in the vicinity of the ionic source of a mass spectrometer. Their experiments have shown that during the cleavage of inorganic crystals (calcite, magnesite, cerussite, lead and sodium azides) gas evolution can be substantial, which suggests, in Fox's opinion, that high temperatures exist at the crack tip.

However, since in brittle substances the rate of crack propagation can approach the sound velocity, i.e. 10^3 m/s, the life time of excitation on the chemical bond must be 10^{-13} s. It is evident that under this condition the term temperature can be used only symbolically. Another, not very well proved part of Fox and Loria-Rutz's work is the suggestion that the chemical process occurs within a monomolecular layer on the surface of the clefts nearby the crack tip. Besides, the salts studied by Fox and Loria-Rutz's always decompose by one and the same mechanism. Taking this into account, in a study carried out at our Institute in collaboration with the Ioffe Physico-Technical Institute, we have chosen as the subject of our study the nitrates and bromates of alkali metals which can decompose by two parallel routes. Therefore, by following the composition of the gas evolved during the course of crystal cleavage, one might hope to make a conclusion about the mechanism of processes occurring at the tip of a moving crack. The results of the experiments have shown that depending on the rate of crack propagation, the composition of the gaseous products changes. At the first instant, as the crack accelerates, oxygen is evolved and further the increase in the speed of crack motion is accompanied by the evolution of nitrogen oxide as the main product [7,8].

Thus the processes occurring at the tip of a crack during the cleavage of a crystal may proceed by different mechanisms depending on the speed of crack motion [9]. This led us [10] to suppose that here we have a unique case of excitation of high vibro-levels of chemical bonds which influence the mechanism of chemical reactions of solids [11-13]. Recently, when conducting investigations of the processes occurring at the tip of a crack, Dickinson et al. [14,15] have obtained some interesting results which support, in our opinion, our understanding of the specific character of the processes occurring at the crack tip.

3. Preliminary mechanical activation

The high-energy excited states occurring in a solid as a result of mechanical treatment are not necessarily short-lived, as is the case in the above example of crack propagation. Mechanical activation can also

lead to the occurrence of metastable states the lifetime of which is much more than the time of reaction. In this case it is customary to speak about preliminary activation.

For a long time it has been assumed that the main cause of change of the reactivity is the formation of a new surface during the mechanical treatment. However, the experiments of Schrader et al. [16] have shown that the correlation between the reactivity and increase in the surface during the grinding of various powders in vibratory mills does not always exist. Moreover, sometimes, this factor accounts for only several percent of the overall effect of increase in reactivity. Analogous results have been also obtained by other researchers.

However, the suggestion that the reactivity of a solid is determined by the total content of defects in the crystal has also required revision and refinement. It turned out that the real structure of a crystal and the concentrations of defects cannot be judged using such integral characteristics as excess enthalpy or the half-width of the line on an X-ray pattern.

When characterizing the reactivity, not all the defects existing in the crystal should be taken into account, but only those which directly or indirectly take part in the chemical reaction [16]. In other words, when estimating the effect of various kinds of treatment on the reactivity of solids, one should take into account the influence of not all of the defects, but only those to which the reaction is most sensitive [17].

As an example, consider the dissolution of sodium fluoride in water after mechanical treatment [18]. A calorimetric study conducted during the mechanical activation of sodium fluoride has shown that during the course of the process fluoride crystals accumulate excess energy. This energy is considerably larger than its increment due to the increased surface. The fluoride activated in such a way dissolves in its own saturated solution, producing a supersaturation of up to 5% with respect to sodium fluoride. As the absolute values of the energy excess are within the limits of 1 kJ per mole, this exceeds about two times the energy that could be expected if the main source of its accumulation in the crystal is dislocations at their maximum concentration ($10^{12}/\text{cm}^2$). A more detailed study of the properties of the activated fluoride has shown that dislocations form at

the very beginning of mechanical activation. After the dislocations have formed, a strong increase in the concentration of point defects occurs in the crystal, and at later stages of activation this factor is the main one. Such a sequence in the accumulation of defects during the activation of fluoride affects its physico-chemical properties. Thus during the dissolution of sodium fluoride in ethanol it has been observed that the specific rate of dissolution of crystals plotted against the value of accumulated energy passes through a maximum. A considerable increase in the rate is observed only at the initial stage of activation when dislocations, i.e. the defects to which the dissolution is sensitive are accumulated. Further, the rate of dissolution slows down despite the steady rise in the amount of accumulated energy. These stages involve the formation of a sub-surface layer of the shell of the fluoride with a high concentration of point defects. This layer blocks dislocations and therefore the rate of dissolution of the fluoride decreases. As is well known the rate of dissolution, as well as every heterogeneous process is determined, on the one hand, by the value of rate constant per unit of the interface between the dissolved substance and the solvent, and on the other hand, by the geometric conditions of the progress of the reaction producing a change in the interface value itself. A change in the density of dislocations has an effect on both of these factors (in contrast to a change in the concentration or the type of point defects or a change in habitus which affects one of these factors). Therefore the dissolution processes are so sensitive to the presence of dislocations in the crystal and the substitution of this type of defect by another, even if from the surface, that it will produce a decrease in the rate of the reaction.

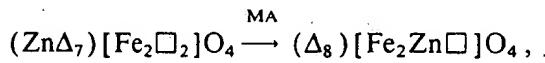
A more complicated situation occurs during the mechanical activation of complex oxides and sulphides. As is known [19], in the structures of these compounds the close packing of the anion is different for ferrite-spinels and for orthoferrites.

In the structure of ferrite-spinels, MeFe_2O_4 , the oxygen anions are in close packing and the bi- and trivalent cations occupy octahedral and tetrahedral vacancies in the lattice. In orthoferrites (the perovskite structure) the large size cations take part in the formation of a cubic close packing and the Fe^{3+} cations occupy octahedral vacancies. No positions

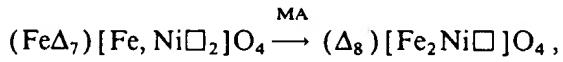
tetrahedrally coordinated by anions are available in this structure.

During the mechanical activation of both ferrite-spinels and orthoferrite, the process of activation is not restricted to a simple increase in the concentration of linear or point defects as is the case with simple binary compounds (sodium fluoride, for example). A characteristic property of the activation of these oxides is that on reaching a certain degree of disordering they undergo qualitative changes in the structure, namely, changes of short-range order. The structure of ferrite-spinels is such that there is the possibility of polytypism of the anion sublattice involving a change in the arrangement of the cations over tetra and octa vacancies. This determines the most probable ways in which the structure of ferrites can change during mechanical activation.

According to Mössbauer spectroscopy data, one of the main features of the mechanically activated ferrites is that at room temperature they are paramagnetic and have a value of the chemical shift of 0.35 ± 0.01 mm/s which is characteristic of iron in octahedral coordination. The mechanical activation of both direct and inverse spinels results in the formation of substances in which tetrahedral vacancies are not occupied. For instance, in the ferrites of nickel and zinc, the cation exchange occurs between the tetra and octa vacancies, which leads to a change in the degree of inversion:



whereas in the ferrites of Mn and Ni the cation exchange proceeds by the scheme:



(Here the unoccupied tetra and octa vacancies in the close-packed oxygen sublattice are designated as Δ and \Box , respectively, MA is the mechanical activation.) At the same time, X-ray diffraction data show that during the course of mechanical activation, despite the slight distortions of the structures apparently associated with the absence of cations in the tetra positions, the long-range order is retained [20-23]. A characteristic feature of the mechanical activation of ferrite-spinels is a threshold character of the process with respect to the power of the energy delivered. In other words, the effect is observed only

in the case if the energy intensity of the mechanical activator becomes higher than the value characteristic of the given system. The substances obtained by activation possess properties untypical of unactivated substances. For instance, the Néel temperature of 90 K for zinc ferrite increases to 210 K after activation. The changes in the physical properties are accompanied by changes in the chemical ones. For example, the mechanical activation of zinc ferrite brings about a change in the order of leaching of zinc and iron cations during treatment with acid [24]. According to the model proposed, the initial stage of activation of ferrite-spinels is connected with the presence of shear in the oxygen sublattice after activation. Some of these shears in the (111) direction correspond to certain distortions in the oxygen packing. For example, a hexagonal close packing is wedged between the layers a face-centred cubic one. The changes in the anion sublattice lead to a redistribution of the ions in the cation sublattice. The value of the specific surface does not change therewith. The observed state is metastable and the spinel may be returned to the initial state by simple annealing. An investigation of the radial distribution function for the mechanically treated and untreated spinel has shown that the short-range order remains unchanged [23]. This also agrees with high-resolution electron microscopy data [25], according to which during the mechanical activation of ferrite spinel, the crystalline blocks of the lattice increase in size, i.e. no disordering and amorphization of the lattice occurs, indicating that not a "disorganization" of the structure takes place, but on the contrary, self organization.

In the case of the perovskite structure, translations in the close-packed anion sublattice are forbidden and during activation one should expect primary distortions of the initial structure and, first of all, a decrease in the symmetry of the $[FeO_6]^{9-}$ octahedron with the transformation of it into an elongated tetragonal pyramide, a displacement of the Fe^{3+} from the centre of the octahedron, or rotations of the $[FeO_6]^{9-}$ octahedra in the lattice sites. The Mössbauer spectra of activated perovskites indicate a decrease in the coordination number of the iron cations during the course of activation. Another peculiarity of the activation of perovskites is a decrease in the short-range order during the course of activation and finally a complete amorphization of

the activated perovskite. The cause of such a behaviour of the perovskite structure during activation appears to be the fact that despite of the potential possibility of polytypism for the packing of MeO_3 layers, the strong repulsion of the tricharged cations prevents the shears of the (111) type planes. Therefore, the shearing deformation of the lattice inevitably results in the disturbance of the short-range and long-range order.

Thus, the activation of both the spinel ferrites and orthoferrites involves shears during the plastic deformation of the crystal, and the difference in the nature of the activated state between them is due to the possibility of retaining symmetry in the oxygen sublattice during deformation in ferrite-spins and the disturbance of it in perovskites. Analogous results have been obtained for compounds in which the sulphur atoms are in close packing. Thus, for instance, the mechanical activation of chalcopyrite leads to analogous changes in the physical and chemical properties occurring as a result of shearing processes in the hexagonal sulphur sublattice [26].

The mechanical activation of composite intermetallic compounds leads to the formation of such exotic defects as a quasi-crystalline structure. It has been shown that during the process of mechanical treatment of cubic $\text{Mg}_{32}(\text{Zn}, \text{Al})_{49}$ crystals, the icosahedral phase forms locally owing to the formation of rotation defects and the disorder of the crystal planes occurs due to the action of plastic deformation. The process develops via a mechanism similar to nuclei growth, i.e. the size of the disordered regions in the icosahedral phase increases with increasing time of mechanical treatment [27].

4. Mechanical stresses occurring in a solid during the course of reaction. Their role in the subsequent progress of the process

In the above examples, the influence on mechanical treatment from an external field was studied. A particular situation occurs when a stress field forms in the crystal due to the reaction itself. This case is a kind of feed-back typical of solid state chemical reactions.

The main idea of this and similar studies is that a complex of factors rather than one single factor may

be responsible for the feed-back. One of the most common factors responsible for autolocalization of a solid state reaction is the generation of mechanical stresses at the reactant/product interface. A model study illustrating the role of this factor in a very clear and simple way has been recently carried out by A.A. Sidelnikov in my Laboratory. He has studied the process of water loss by silica glue, i.e. the dehydration of a gel of sodium silicate. During the course of dehydration of this system, mechanical stresses arise due to the formation of water vacancies in the surface layer. As a result of stress relaxation, a crack is formed; this crack plays now the role of a new surface. New cracks are formed in the vicinity of the first one and as a result, nucleation can be observed.

The phase transition of NH_4Cl can be cited as another example [28]. Due to the difference in the molar volume of and polymorphs, mechanical stress arises. An analysis of the phase diagrams has shown that the increase in the stress must inhibit the transition. However this stress relaxes via punching of dislocation semi-loops slipping from the interface into the volume of the parent crystal. As a pile-up of dislocation loops are formed, the back stress from a pile-up on the nucleus prevents the formation of a new semi-loop. As a result, the stress relaxation becomes hindered and the growth of the nucleus stops. Besides, a very interesting effect is observed, necessitating a revision of one of the dogmas of formal topokinetics. It has been found that during the subsequent appearance of nuclei, each nucleus of phase appearing earlier creates a stress field in the crystal and thereby decelerates not only the formation but also the growth of every subsequent nucleus.

During the thermal decomposition of ammonium perchlorate, at least two possible processes responsible for the process of autolocalization may be considered. First, thermal decomposition starts at dislocation. Therefore, the first molecules of NH_3 and HClO_4 form not at the surface but in the subsurface layer. A gaseous bulb is formed inside the parent crystal and as a result, mechanical stress arises. The relaxation of mechanical stress produces new dislocations which act as new centres where the further reaction occurs [29]. Second, we have shown that perchloric acid HClO_4 is accumulated in a micropore, since smaller and lighter NH_3 molecules leave this micropore more easily. As the concentration of

protons in a pore increases, their migration to the dislocation in the vicinity of the pore becomes effective and thus dislocations newly injected by protons become new reaction centres, form new pores, etc. [30].

From the above examples which can be continued (see for instance ref. [31]), it follows that mechanical stresses occurring during the course of reaction may play a significant role in the progress of solid state chemical processes. From this it is clear why a detailed investigation of the nature of a feed-back via mechanical stresses during the course of a topochemical reaction is extremely necessary for an understanding of the mechanism of this process and for a search of a method whereby it can be controlled. Possible practical application also requires this, since on the one hand the character of stresses at the starting substance/product interface largely determines the properties of the product. On the other hand, to use expensive mechanical energy only for the initiation of the process and then make the process use its own mechanic energy for its development has always been a very attractive problem for technologists.

Since the processes involving feed-back occur mainly near by the starting substance/reaction products interface, a study of structural changes at the interface is of particular significance. We have used synchrotron X-ray radiation for investigation of structural changes which occur in the reaction interface area. As is well known, synchrotron radiation is many times brighter than commonly used X-ray radiation in usual X-ray tubes. Therefore, the time of diffraction experiments and the size of the sample are under investigation can be reduced to 10^{-3} – 10^{-4} s and $1 \mu \text{m}^2$, respectively. This allowed the use of two variants of experiment to study structural distortions at the interface. In the first variant, a position-sensitive one-coordinate X-ray detector was employed. A special device made possible scanning of the crystal, starting from the region of the parent phase on to the product nuclei. A certain diffraction maximum was prechosen and then the halfwidth, intensity, shape and position of this maximum were studied. We carried out the experiments on crystalline hydrates. Structural distortions were observed in the reactant phase rather far from the visible boundary. The width of the interface was estimated

to be 150–200 μm , depending on the experimental condition of dehydration [32].

The second variant of the experiment was based on the use of a two-coordinate detector and polychromatic synchrotron X-ray radiation. In this case not only new information concerning the width of the reaction interface was obtained but also the details of relaxation of mechanical stresses at the interface and the textural and morphological characteristics of the product formed were established [33].

5. Activation in solid-solid systems

To understand the physics and chemistry of the process in mechanically-treated solid mixtures, it is necessary to consider what is the interface between solids. The main characteristic feature of these systems is the change of the properties of the crystal in the area of contact between the solid components [34]. When two phases are brought into contact, the properties of both are changed. Among these changes, the following are worth noting:

(a) The distortion of crystal structures of contacting solids due to the misfits or as a consequence of the fixation of plastic deformation. This kind of deformation is common during mechanical alloying of metals. The depth of distorted interface can vary in a very wide range from several interatomic distances to several microns.

(b) Redistribution of electrons at contact between solids with different work functions. The depth of this region with changed electron concentration depends on the contact potential difference and electronic level density and can vary from nanometers to microns.

(c) Redistribution of point defects at the interface (C. Wagner's effect). The depth of this layer is evaluated to be between ten to hundreds nanometers.

When the particle size of the contacting components is much larger than the depth of the layer with the changed properties, the change in the physico-chemical properties of the components in the contact area can be neglected. This is usually done in conventional techniques of grinding and mixing. However, during hyperfine grinding which proceeds to a level of several microns it is possible to obtain a composite in which the particle size is of the same

order a
erties.
tained
erties o
it poss
as hyd
lysts.
In i
lution
region
fusion
Also,
mixtu
tacts.
react:
temp:
tinuo
the re
cess f
a cer
high-
tions
ester
tion,
accel
chan

Refer

- [1] K A
- [2] V
- [3] V
- [4] V
- [5] V
- [6] V
- [7] V
- [8] I
- [9] I
- [10] V
- [11] V
- [12] V
- [13] V
- [14] V

order as the width of the layer with changed properties. The properties of mechanocomposites obtained in such a way differ sharply from the properties of the starting components. This method makes it possible to obtain new alloys which can function as hydrogen accumulators, new highly active catalysts, fast ionic conductors, etc. [35-37].

In the cases where the components form solid solutions, a chemical interaction can proceed, i.e. the region of contact becomes the region of mutual diffusion of components or the chemical reaction zone. Also, in this case, the mechanical treatment of the mixture produces an increase in the number of contacts, an increase in the area of contact between the reactant, and a local increase in the pressure and temperature at the site of the contact. Besides, continuous removal of the formed solid product from the reaction zone and therefore the return of the process from diffusion to the kinetic regime may be of a certain significance. The synthesis of some ferrites, high-temperature superconductors and some reactions between organic solids (halogen substitution, ester formation, reduction, hydrogenation, oxidation, etc.) may be cited as an example illustrating the acceleration of the reaction between solids upon mechanical treatment [38-40].

References

- [1] K. Tkacova, *Mechanical Activation of Minerals* (Elsevier, Amsterdam, 1989) p. 26.
- [2] V. Boldyrev and A. Medvinsky, *Kinet. Catal.* 6 (1965) 550.
- [3] V. Boldyrev, *Intern. J. Radiat. Chem.* 3 (1971) 155.
- [4] V. Boldyrev, J. Zarko and A. Deribas, *Chem. High Energy* 1 (1967) 117.
- [5] V. Boldyrev, E. Awwakumov, H. Harenz, G. Heinicke and L. Strugova, *Z. Anorg. Allg. Chem.* 393 (1972) 152.
- [6] P. Fox and J. Loria-Rutz, *Proc. Roy. Soc. A* 317 (1970) 79.
- [7] V. Boldyrev, V. Regel, F. Urakaev and O. Pozdnjakov, *Dokl. Akad. Nauk SSSR* 221 (1975) 634.
- [8] F. Urakaev, V. Boldyrev, O. Pozdnjakov and V. Regel, *Kinet. Catal.* 18 (1977) 350.
- [9] V. Boldyrev, N. Lyakhov, Y. Pavlyukhin, E. Boldyreva, E. Ivanov and E. Awwakumov, *Sov. Sci. Rev. B. Chem.* 14 (1990) 126.
- [10] V. Boldyrev, *Kinet. Catal.* 13 (1972) 1411.
- [11] V. Boldyrev and G. Heinicke, *Z. Chem.* 19 (1979) 353.
- [12] M. Eberhart, R.M. Latanision and K.M. Johnson, *Acta Metallurg.* 33 (1985) 1769.
- [13] B. Lawn, *J. Am. Ceram. Soc.* 66 (1983) 83.
- [14] J.T. Dickinson, L.C. Jensen, M.R. McKay and F. Freund, *J. Vac. Techn. A* 4 (1986) 1648.
- [15] J.T. Dickinson, L.C. Jensen, I. Langford and J. Hirth, *J. Mater. Res.* 6 (1991) 112.
- [16] R. Schrader and B. Hoffman, in: *Festkörperchemie. Beiträge aus Forschung und Praxis*, V. Boldyrev and K. Meyer, eds. (Grundstoffindustrie, Leipzig, 1973) p. 528.
- [17] V.V. Boldyrev, M. Bulens and B. Delmon, *The Control of the Reactivity of Solids* (Elsevier, Amsterdam, 1979) pp. 16-30.
- [18] E. Goldberg and A. Eremin, *Proc. Siber. Acad. Sci. USSR, Ser. Chim.* 5 (1985) 2.
- [19] A. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, 1986) p. 213.
- [20] Y. Pavlyukhin, Y. Medikov and V. Boldyrev, *Mater. Res. Bull.* 18 (1983) 630.
- [21] Y.T. Pavlyukhin, Y. Medikov and V. Boldyrev, *J. Solid State Chem.* 3 (1984) 155.
- [22] Y.T. Pavlyukhin and V. Boldyrev, *Rev. Solid State Sci.* 2 (1988) 603.
- [23] A. Rykov, Y. Pavlyukhin, N. Sirotina and V. Boldyrev, *React. Solids* 7 (1989) 29.
- [24] V. Boldyrev, O. Yakovleva, Y. Medikov and Y. Pavlyukhin, *Dokl. Acad. Nauk SSSR* 226 (1983) 636.
- [25] B. Bokhonov, S. Paramzin et al., *J. Mat. Proc. Synth.* 1 (1993).
- [26] K. Tkacova, V. Boldyrev and Y. Pavlyukhin, *Proc. Siber. Acad. Sci. USSR, Ser. Chim.* 4 (1984) 4.
- [27] B. Bokhonov, I. Konstanchuk, E. Ivanov and V. Boldyrev, *J. Alloys Compounds* 187 (1992) 207.
- [28] A. Chupakhin, A.A. Sidelnikov and V.V. Boldyrev, *React. Solids* 3 (1987) 1.
- [29] A.V. Rajevsky, in: *Mechanism of Thermal Decomposition of Ammonium Perchlorate* (Inst. Chem. Phys., Chernogolovka, 1981).
- [30] V.V. Boldyrev, Y. Savintzev and T. Mulina, *Reactivity of Solids*, Proc. 7th Intern. Symp., Bristol (Chapman and Hall, London, 1972) p. 237.
- [31] V.V. Boldyrev and E. Ivanov, *Kinet. Catal.* 17 (1976) 1447.
- [32] V.V. Boldyrev, Y. Gaponov, N. Lyakhov, A. Politov and B. Tolochko, *Nucl. Instrum. Methods Phys. Res. A* 261 (1987) 192.
- [33] Y. Gaponov, N. Lyakhov, B. Tolochko, V. Boldyrev and H. Scheromov, *Nucl. Instrum. Methods Phys. Res. A* 282 (1989) 648.
- [34] V.V. Boldyrev and E.V. Boldyreva, *Mater. Sci. Forum* 88-90 (1992) 703.
- [35] I. Konstanchuk, E. Ivanov, M. Pezat, B. Darriet, V. Boldyrev and P. Hagenmuller, *J. Less Common Met.* 131 (1987) 181.
- [36] E. Ivanov, T. Grigorjeva and G. Golubkova, *Mater. Lett.* 7 (1988) 55.
- [37] G.F. Hairetdinov and E. Ivanov, *Mater. Sci. Forum* 88-90 (1992) 723.
- [38] N. Hainovsky, Y. Pavlyukhin and V.V. Boldyrev, *Mater. Sci. Eng.* 88 (1991) 283.
- [39] A. Dushkin, E.V. Nagovitsina, V. Boldyrev and A. Druganov, *Proc. 3rd Soviet-Japan Symp. on Mechanochemistry* (Russian Acad. Sci., Novosibirsk, 1991) pp. 75-82.
- [40] V.B. Chuev and L.A. Lyagina, *Siber. Chem. J.* 1 (1991) 133.

The Fundamentals of Mechanochemical Processing

P.G. McCormick and F.H. Froes

It has been demonstrated that the activation of chemical reactions by mechanical energy can lead to many interesting applications, ranging from waste processing to the production of advanced materials with novel microstructures and enhanced mechanical properties. In this article, the status of three types of mechanochemical processing is reviewed—mechanical milling, mechanical alloying, and reaction milling.

INTRODUCTION

Mechanochemical processes (MCP) use mechanical energy to activate chemical reactions and structural changes. However, these are not new processes; mechanically activated processes date back to the early history of humankind (e.g., the use of flints to initiate fires). Following these early uses, the field of mechanochemistry has had a rich history, particularly in Europe, which has led to the use of ball mills for processing a wide range of materials, ranging from minerals to advanced materials.

In this review, the status of three different types of mechanochemical processes is discussed: mechanical milling (MM), mechanical alloying (MA), and reaction milling (RM). MM refers to the milling of a pure metal or compound that is in a state of thermodynamic equilibrium at the start of milling. MA refers specifically to the formation of alloys from elemental precursors during processing in a ball mill. RM uses mechanical processing to induce chemical reactions. The principal attributes of mechanochemical processing include mineral and waste processing, metals refining, combustion reactions, ultrafine powder production, production of a fine disper-

sion of second-phase particles, extension of solubility limits, refinement of the matrix microstructure/nanograin formation, synthesis of novel crystalline phases, formation of amorphous phases, the possibility of alloying difficult-to-alloy elements, and scaleability.¹⁻⁵

Solid-state reactions, whether alloying or chemical reactions, involve the formation of one or more product phases that separate the reactants. Diffusion through the product phases is invariably the rate-controlling process, and, consequently, high temperatures are normally required to achieve acceptable reaction kinetics. MCP overcomes this diffusion limitation, with the metastable structures developed directly reflecting the diffusion constraints imposed by the low-temperature nature of the process.

The departure from equilibrium that is possible using MCP is shown in comparison with a number of other far from equilibrium processes in Table I.³ The departure possible using vapor-phase processing is greater than that for MCP; but, in comparison, MCP allows greater excursions than rapid solidification (RS).

An important feature of MCP is the refinement of microstructure (i.e., grain size and particle size) associated with particle deformation, fracture, and welding processes that accompany ball/powder collision events. The energy transmitted to crystalline powders during milling results in a dislocation cell structure that develops into random nanostructured grains with increasing milling time. While nanometer grain sizes are developed during MCP, powder particle sizes generally decrease only to

the micrometer level.

MCP can also result in extended solid solubility, disordering, and the formation of amorphous structures. Schwarz et al.⁶ have shown that such high-solubility enhancements can be rationalized in terms of a metastable equilibrium between the solid solution and a solute-rich amorphous phase.

A significant research effort has been devoted to studies of mechanically induced amorphization reactions over the past ten years.⁷⁻⁹ It appears that for amorphous phases to form during MM, the increase in energy of the milled powder, which is mainly due to the increased volume fraction of grain boundaries and disordering, must raise the free energy to above the level of the amorphous state.^{9,10}

The formation of metastable crystalline phases during MCP has been reported by a number of researchers.¹¹⁻¹³ For example, Han et al.¹¹ reported the formation of metastable phases during the mechanical milling of rare-earth sesquisulfide phases.

It has been shown that mechanical activation substantially increases the kinetics of solid-state chemical reactions, such as oxidation-reduction reactions.⁶ During milling, the reaction zones not only increase as particle and grain sizes decrease, but are also regenerated through the repeated particle fracture and welding events. As a consequence, reactions that, due to the separation of the reacting phases by the product phases, require high temperatures to occur, will occur at low temperatures in a ball mill without any need for external

Table I. Departure from Equilibrium Achieved in Various Processes³

Process	Max. Departure from Equilibrium (kJ/N _A) [*]
Solid-State Quench	16
Quench from Liquid (Rapid Solidification)	24
Condensation from Vapor	160
Irradiation/Ion Implantation	30
Mechanical Cold Work	11
Mechanical Alloying	30

^{*}—Avogadro's number.
i.e., assuming no relaxation due to kinetic effects.

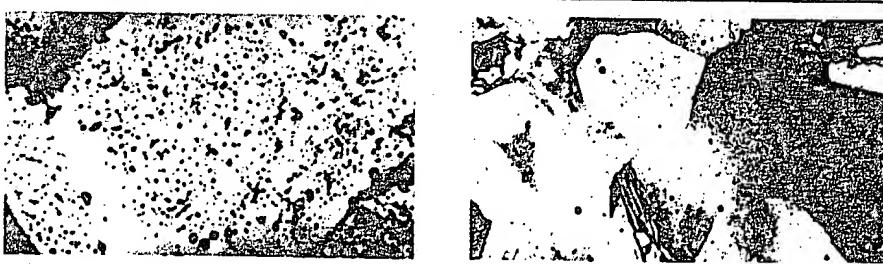


Figure 1. Transmission electron micrographs of dispersoids in (a) RS Ti₃Al-2 Er alloy HIPed at 850°C and (b) MA Ti₃Al-20Nb-2Mo-3V-2Er alloy HIPed at 1,000°C. Note the fine grain size and small size of the dispersoid in the MA alloy even after HIPing at a higher temperature. Note also the presence of dispersoid-free zones in the RS alloy and their absence in the MA alloy.¹⁻⁵

Table II. Nominal Compositions of Major Mechanically Alloyed Materials

Alloy	Ni	Fe	Cr	Al	Ti	Mo	W	Ta	Y ₂ O ₃
Inconel MA 956	—	Bal.	20	4.5	0.5	—	—	—	0.5
Inconel MA 957	—	Bal.	14	—	1.0	0.3	—	—	0.25
Inconel MA 754	Bal.	—	20	0.3	0.5	—	—	—	0.6
Inconel MA 758	Bal.	—	30	0.3	0.5	—	—	—	0.6
Inconel MA 6000	Bal.	—	15	4.5	2.5	2.0	4	2	1.1
Inconel MA 760	Bal.	—	20	6.0	—	2.0	3.5	—	0.95

heating. Thus, the ball mill may be considered to be a chemical reactor in which a wide range of chemical reactions can be mechanically initiated.

MINERAL AND WASTE PROCESSING

The mechanical activation of minerals was one of the earliest applications of MCP.¹⁵ The ultrafine grinding of minerals, such as chalcopyrite or sphalerite, is well known to increase chemical reactivity so that the valuable constituents can be leached under far less severe conditions than would normally be required. For example, it has been shown that the mechanical activation of refractory pyrite and arsenopyrite enables the extraction of gold via low-temperature pressure oxidation.¹⁶ Although not extraction, the use of ultrafine grinding to mechanically activate fly ash improves pozzolanic reactivity.¹⁷

Recent studies have shown that chemical reactions can be initiated by grinding minerals with appropriate reactants that enable selective removal of the valuable constituent. For example, the mechanochemical reaction between chalcopyrite (CuFeS₂) and CuO results in the selective formation of CuSO₄, enabling the removal of copper by simple water leaching.¹⁸ Other minerals and mineral wastes that have been successfully treated include pyrite, arsenopyrite, monazite, bauxite, and red mud.

MCP has also been successfully applied to the destruction of intractable organochlorines, such as polychlorinated biphenyls and dichlorodiphenyltrichloroethane.^{19,20} Mechanochemical reactions between the organochlorine and calcium oxide or other suitable reactants are activated in a ball mill and result in the

destruction of the molecular structure of the toxic material and the formation of inorganic chlorides. The process has been shown to be applicable to the destruction of a wide range of toxic materials.

METALS REFINING

A wide variety of oxidation-reduction reactions can be activated during the MM of an oxide of chloride with a suitable reductant. For example, milling CuO with a reductant such as calcium results in the reduction of the cupric oxide to copper metal.¹⁴ Cobalt-reduction processes to directly form alloys, such as the formation of brass from CuO and ZnO by milling with calcium, have also been reported. Examples of potentially important refining reactions include the reduction of TiCl₄ with magnesium^{21,22} and the formation of rare-earth permanent magnet alloys by reduction reactions with calcium or sodium.^{23,24}

The microstructure of the as-milled powders consists of a nanocomposite mixture of the product phases, with 5–20 nm crystallites of the reduced metallic phase being uniformly intermixed with an amorphous or nanocrystalline by-product phase. The separation or removal of unwanted reaction by-product phases can be difficult due to the high reactivity of the metallic phase associated with its nanocrystalline grain size, intermixing of the phases induced by the MM process, or limited solubility of the by-product phase. The use of carbon as the reductant obviates the need to remove the reaction by-products, since gaseous CO₂ is formed by the reaction.²⁵ Alternatively, by appropriate selection of the reaction chemistry it may be possible to form by-product phases, such as chlorides, which are soluble in inert li-

uids or may be removed by vacuum distillation.

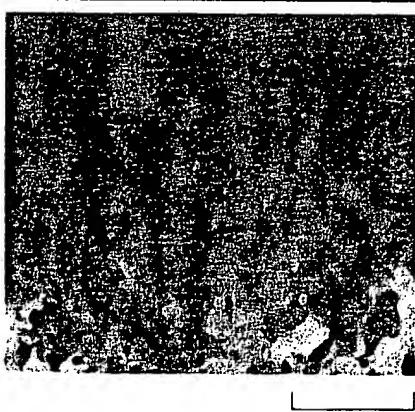
The TiCl₄/Mg reaction is also of interest because TiCl₄ is a liquid at room temperature and, thus, is an example of the mechanical activation of a liquid-solid reaction. It has been shown that decreasing the milling temperature so that TiCl₄ becomes solid increases the reaction kinetics by a factor of six, demonstrating the importance of solid-solid interactions at welded interfaces during milling.²¹

THE PRODUCTION OF SECOND-PHASE DISPERSIONS

The MA process was initially developed in the late 1960s to combine the intermediate temperature strength of the γ precipitate with the high-temperature dispersion hardening in nickel-based alloys.^{26,27} This is presently the major use of the process.²⁸ The major commercial dispersion-strengthened nickel-based alloys produced are the Inconel alloys, which contain substantial amounts of chromium and aluminum to impart resistance to environmental attack by providing a homogeneous distribution of the alloying elements and an improved scale adherence (Table II). The stress-rupture properties of MA 6000 exceed those of competing alloys above 900°C.^{26–29} and MA 760 and MA 6000 alloys retain rupture strengths higher than those of TD-nickel and directionally solidified MAR-M200 + Hf alloys.²⁹

Several iron-based high-temperature alloys have also been produced by MA techniques.²⁶ Inconel MA 956 (Table II) can be used at operating temperatures higher than 1,300°C in corrosive atmospheres, especially in carburizing or sulfidizing environments. This alloy is fabricable and is presently used as a sheet material for aircraft and industrial gas turbine combustors and in swirlers and heat exchangers of power-generation equipment.

The MA of aluminum-based alloys leads to a higher temperature capability than similar RS-processed materials.²⁷ The additional improvement results



a

200 nm



b

200 nm



c

200 nm

Figure 2. Transmission electron micrographs of TiAl nanograins in material mechanically alloyed and HIPed at (a) 725°C, (b) 850°C, and (c) 975°C.

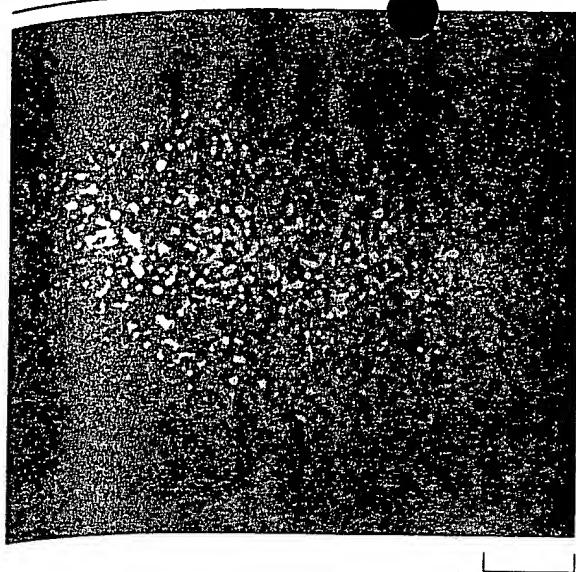


Figure 3. An as-milled particle containing the nanodispersion of nickel in an NaCl matrix.

from the formation of fine Al_2O_3 and Al_2C dispersoids (due to the addition of organic process control additives and the presence of ambient oxygen in the milling atmosphere).

The dispersoids formed in MA alloys are very fine and uniformly distributed; both the grains and dispersoids do not coarsen considerably even on very high-temperature exposure to temperatures up to 1,100°C.²⁸ Figure 1 shows that both the grain and dispersoid sizes are much finer in the MA $\text{Ti}_3\text{Al} = 2\text{Er}$ alloy, even though this was hot isostatically pressed (HIPed) at 1,000°C, a temperature 150°C higher than the HIPing temperature for the RS alloy.²⁹

Currently, the specialty market of oxide-dispersion strengthened (ODS) superalloys is about 350 tons per year at the commercial output level. The cost of the MA process step is held proprietary by the producer (Inco), but is probably about \$5 per pound for an eight-hour MA cycle.

SOLID-SOLUBILITY EXTENSION

Some solubility extensions in the aluminum system obtained by MA and the corresponding values developed using RS, where available, are listed in Table III. These are the solubility levels obtained in terminal solid solutions; little data is available on the intermetallics.

MA should generally allow even greater solid-solubility extension (SSE) than RS (Table I).³ Schwarz et al.⁶ suggested that this SSE could be rationalized in terms of the metastable equilibrium between the terminal solid solution and an amorphous phase rather than the stable equilibrium between the terminal solid solution and an intermetallic. This explanation appears to hold true for a variety of systems.

NANOSTRUCTURED GRAINS

The large amount of energy transmitted to MA powders results in a dislocation cell structure within shear bands, which transforms to random nanostructured grains with increasing MA time.^{30,31} In the Ti-Al system, the crystal size in the MA powder decreased exponentially with milling time and reached nanometer levels in less than one hour; decreased milling intensity (lower ball-to-powder ratio) resulted in a slower decrease in the crystal size. The presence of the nanostructured grains was confirmed by

transmission electron microscopy (Figure 2).³² The minimum (saturation) grain size formed, which occurs prior to amorphization in some cases, decreases as the intensity of milling is increased, as confirmed in other work.³¹

PHASE FORMATION

Amorphous

The discovery by Koch et al.⁷ that MA can result in the formation of amorphous structures was an important breakthrough, and a significant research effort has been devoted to studies of mechanically induced amorphization reactions during the past ten years.^{8,9} It appears that it is the increase in energy mainly due to an increased volume fraction of grain boundaries and disordering^{3,10} that raises the free energy of the initially ordered compound to above the level of the amorphous state. For this to happen, the amorphous state must be such that when the two elements mix in the amorphous state, there must be a large negative heat of mixing.³² This free energy in the MA condition must also be lower than that for a mixture of the crystalline components of the two elements. In some cases, the Miedema model^{12,13} gives a good comparison between experimental and theoretical data.

Novel

Han et al.^{11,12} have reported the formation of metastable phases during the MM

of rare-earth sesquisulfide phases. Mechanical milling $\alpha\text{-Dy}_2\text{S}_3$ (orthorhombic) for one hour resulted in the formation of the cubic-high temperature γ phase, normally stable at temperatures in excess of 1,463 K. A similar transformation was observed in milled copper-doped h (U_{2-x} -type) Dy_2S_3 , $\text{Cu}_x(\text{Dy}_2\text{S}_3)_{1-x}$, with $x=0-0.15$. Hot pressing at 1,373 K caused a transformation back to the equilibrium phase, with the exception of samples having the composition $\text{Cu}_{0.023}(\text{Dy}_2\text{S}_3)_{0.975}$, where the Gd_2S_3 -type α -orthorhombic phase formed instead.¹²

Mechanical milling of monoclinic $\delta\text{-Y}_2\text{S}_3$, $\delta\text{-Er}_2\text{S}_3$, and $\delta\text{-Tm}_2\text{S}_3$ caused the formation of their respective cubic γ high-pressure polymorphs. With rhombohedral Yb_2S_3 and $\epsilon\text{-Lu}_2\text{S}_3$, milling for up to 40 h resulted in only a partial transformation to their respective high-pressure γ polymorphs. Hot pressing of MM $\eta\text{-Y}_2\text{S}_3$ caused the structure to revert back to the equilibrium δ phase. Ding et al.³⁴ reported the formation of metastable cubic ZrO_2 following reactive milling of ZrCl_4 with CaO .

The formation of metastable phases during the MA of Ce-Yb alloys has been reported by Ivanov et al.¹³ Cerium and ytterbium are immiscible in each other. The MA of mixtures with the compositions of $\text{Ce}_{75}\text{Yb}_{25}$, respectively, resulted in a decrease in the lattice parameter for cerium and the formation of a new face-centered cubic phase with a smaller lattice constant. It was suggested that the decrease in lattice parameter was associated with a change in the valence state of ytterbium from divalent to trivalent during MA.

With increased MA time, a gradual reduction of the long-range order parameter of intermetallics generally occurs,³⁵ this does not always reach total disorder.³⁰ The disordering is a balance between the atomic disordering introduced by the MA and thermally activated ordering.^{32,36} The reordering is caused by the difference in energy between the ordered and disordered state; that is, the more negative (stronger ordering tendency) the ordering energy,^{36,37} the greater the chance of maintaining a degree of order.

In general, the transformation that occurs—amorphization or disordering—will depend on the relative position of the free-energy curves for the ordered compound, the disordered solid solution, and the amorphous state.^{30,32,38} Thus,

Table III. Solid-Solubility Extension by Mechanical Alloying and Rapid Solidification

Solvent	Solute	Solid Solubility (at.%)		
		Equilibrium at RT	RS	MA
Al	Fe	0.025	4.3	4.5
Al	Hf	0.0007	0.3	1.5
Al	Mg	18.9	40	23
Al	Nb	0.065	2.4	>25, <30
Al	Zr	0.015	1.3	6.3

RT—room temperature, RS—rapid solidification, MA—mechanical alloying.



Figure 4. Nanoparticles of nickel formed by a mechanochemical reaction of NiCl_2 with sodium after the removal of NaCl .

in some cases, direct transformation to the amorphous phase will occur (i.e., when the free-energy curve for the amorphous phase is below that for the solid solution). In other cases, the solid solution will form first and as the total energy due to the grain boundaries increases due to a decrease in the grain size, the amorphous phase will form. The type of disordering that occurs may also affect the transformation to either the solid or amorphous phase.³⁸

ULTRAFINE POWDER SYNTHESIS

It has been recently shown that the nanocomposite phase mixtures formed by mechanochemical reactions can be further processed into ultrafine powders with particle sizes as small as 5 nm. A number of transition metals, including Fe, Ni, Co, and Cu; oxides, including Al_2O_3 , ZrO_2 , Fe_2O_3 , and CeO_2 ; and semiconductors, such as ZnS and CdS, have been synthesized by mechanically activated reactions.^{34,39-44}

The precursor powders are milled to form a nanoscale composite structure of the starting phases, which react either during milling or subsequent heat treatment to form a mixture of separated nanocrystals of the desired phase within a soluble matrix. For example, Figure 3 shows an as-milled particle consisting of 5 nm nickel particles embedded in an NaCl matrix that was formed by milling NiCl_2 with sodium.⁴⁵ By controlling the relative volume fractions of the product phases and milling conditions, it is possible to form separated particles of nickel during milling. In particular, the volume fraction of the by-product phase should be sufficiently high so that individual separated particles of the desired phase form via mechanochemical reaction.^{41,45} On dissolution of the soluble phase by a simple washing process after milling, separated nanoparticles of nickel with a narrow particle size distribution

remain (Figure 4).

The synthesis of ultrafine Al_2O_3 and ZrO_2 powders with particle sizes of 10–20 nm has also been reported.^{34,42} To synthesize Al_2O_3 , AlCl_3 , and CaO were milled to form a nanocomposite mixture of CaO particles embedded within an amorphous matrix. The formation of nanoparticles of $\gamma\text{-Al}_2\text{O}_3$ within the CaCl_2 matrix occurred during a subsequent heat treatment at 350°C. Removal of CaCl_2 by washing resulted in $\gamma\text{-Al}_2\text{O}_3$ with a particle size of 10–20 nm,⁴² which transformed to $\alpha\text{-Al}_2\text{O}_3$ on heating to above 1,200°C.

MAGNETS

Permanent

The applications of MA to the synthesis of rare-earth permanent magnets was first demonstrated by the work of Schultz and co-workers.⁴⁶ Subsequently, the magnetic properties of a number of rare-earth transition metal compounds synthesized by MCP have been studied.^{23,24,46–58} Although not yet a commercial process, MCP has received considerable attention in recent years as a candidate process for the commercial manufacture of rare-earth permanent magnets.⁵⁹

Remarkably high values of coercivity, H_c , have been reported, particularly in SmCo_5 , where samples synthesized from SmF_3 have exhibited high values. These alloys are associated with the nanocrystalline grain structure developed by MA and heat treatment, resulting in strong-domain wall pinning at grain boundaries. Wecker et al.⁴⁸ have demonstrated that the use of high-temperature die upsetting following MA and heat treatment can be used to develop texture. Values of maximum energy product, $(\text{BH})_{\text{max}}$, equal to 4.3 MGOe, have been reported in MA and die-upset $\text{Nd}_2\text{Fe}_{14}\text{B}$.

Nanocomposite

Recent studies^{60–68} have demonstrated that MA two-phase rare-earth permanent magnet materials exhibit the phenomena of remanence enhancement associated with exchange coupling at interfaces between nanocrystalline hard and soft magnetic phases. Remanence enhancement enables magnetic materials that are crystallographically isotropic to exhibit remanence values approaching that achieved in fully aligned materials without the necessity of crystallographic alignment.

The nanocrystalline microstructure

inherently developed by MCP appears to be ideally suited to remanence-enhanced magnetic materials. Remanence enhancement is evidenced by high values of remanent magnetization, M_r , relative to the saturation magnetization at high values of the applied field, M_s . Values of M_r/M_s exceeding 0.75 have been reported in several two-phase systems.⁶¹ Such values of M_r/M_s generally require crystallite sizes less than about 20 nm.

CONTAMINATION AND FUTURE TRENDS

The use of MCP in chemical refining allows the direct synthesis of metals and alloys without the need for heating. In principle, MCP alloys allow the three processes—refining, alloying, and powder manufacture—to be carried out in a single low-temperature process. However, in practice, attention must be given to the handling and further processing of highly reactive as-milled powders and the removal of reaction by-products. Much creative work is possible here.

Studies of the MCP of advanced materials, including magnets, have shown that a wide variety of structures, including second-phase dispersions, solubility extension, nanostructured grains, metastable nanocrystalline, and amorphous phases, can be synthesized. The ability to alloy and form phases at low temperatures without melting or high-temperature processing is a unique feature of mechanically activated processing. The low-temperature nature of the process enables disordering and amorphization to occur, with the resulting structures being determined by kinetic rather than thermodynamic considerations. Low-temperature heat treatment of MA structures can also result in the formation of new nonequilibrium phases due to the kinetic constraints of diffusion. Both permanent magnets and nanocomposite magnets with enhanced remanence exhibit attractive behavior. While many of these areas have been explored, much further potential exists. In addition, the application of MCP to waste processing has not yet received much attention, but this is an area worthy of exploration.

Thus, the MCP approach is a potentially useful processing/synthesis technique in a variety of areas. Whether this approach will mature to commercialization, beyond the current ODS superalloys will depend on property improvement levels and cost.

ACKNOWLEDGEMENTS

The authors acknowledge useful discussion with their colleagues, including E.G. Baburaj, J.J. deBarbadillo, J. Ding, G.B. Eranezhuth, P.S. Goodwin, C.C. Koch, R. Street, C. Suryanarayana, R. Schwarz, T. Tsuzuki, and C.M. Ward-Close. We also thank B. Olsen, C. Jackson, and J. Wheeler for their help in manuscript preparation.

References

1. R. Sundareson and F.H. Froes, *JOM*, 39 (8) (1987), p. 22.

2. F.H. Froes, J.J. deBarbadillo, and C. Suryanarayana, *Structural Applications of Mechanical Alloying*, eds. F.H. Froes and J. deBarbadillo (Materials Park, OH: ASM, 1990), p. 1.

3. F.H. Froes et al., *New Techniques in Synthesis and Processing of Advanced Materials*, eds. J. Singh and S.M. Copley (Warrendale, PA: TMS, 1995), p. 1.

4. I.S. Polkin and F.H. Froes, *Int'l. J. of Mats. and Product Tech.*, 10 (1-2) (1995), p. 106.

5. C.M. Ward-Close and F.H. Froes, *JOM*, 46 (1) (1994), p. 28.

6. R.B. Schwarz, R.R. Petrich, and C.K. Saw, *J. Non-Cryst. Solids*, 76 (1989), p. 281.

7. C.C. Koch et al., *Appl. Phys. Lett.*, 43 (1983), p. 1017.

8. A.W. Weber and H. Bakker, *Physica B*, 153 (1988), p. 93.

9. C.C. Koch, *Annu. Rev. Matl. Sci.*, 19 (1989), p. 121.

10. J.S.C. Jand and C.C. Koch, *J. Matl. Res.*, 5 (1990), p. 498.

11. S.H. Han, K.A. Gschneidner, Jr., and B.J. Beaudry, *Scripta Metall. Mater.*, 24 (1991), p. 295.

12. S.H. Han, K.A. Gschneidner, Jr., and B.A. Cook, Jr., *J. Appl. Phys.*, 26 (1994), p. 7899.

13. E. Ivanov et al., *J. Alloys and Compounds*, 198 (1993), p. 105.

14. A.Z. Juhasz and L. Opozny, *Mechanical Activation of Minerals* (New York: Ellis Horwood Ltd., 1990).

15. J.J. Corrals and J.E. Angrove, *Min. Engr.*, 4 (1991), p. 763.

16. S. Lu and U. Ludwig, *Zement Kalk Gips*, 42 (1989), p. 365.

17. H. Yang and P.G. McCormick, unpublished research (1994).

18. A.K. Hall et al., *Nature*, 367 (1994), p. 233.

19. A.K. Hall et al., *Env. Sci. Tech.*, 30 (1996), p. 3401.

20. G.B. Schaffer and P.G. McCormick, *Appl. Phys. Lett.*, 55 (1989), p. 45.

21. P.G. McCormick et al., *Microcomposites and Nanophase Materials*, ed. D.C. Van Aken, G.S. Was, and A.K. Ghosh (Warrendale, PA: TMS, 1991), p. 65.

22. F.H. Froes, "The Production of Low-Cost Titanium Powders," *JOM*, 50 (9) (1998), pp. 41-43.

23. Y. Liu et al., *Appl. Phys. Lett.*, 60 (1992), p. 3186.

24. P.G. McCormick, *Handbook on the Physics and Chemistry of the Rare Earths*, eds. K.A. Gschneidner, Jr., and L. Eyring, 24 (1971), p. 47.

25. H. Yang, G. Nguyen, and P.G. McCormick, *Scripta Metall. Mater.*, 32 (1994), p. 681.

26. J.S. Benjamin, *Met. Trans.*, 1 (1970), p. 2954.

27. J.S. Benjamin, *Sci. Amer.*, 234 (1976), p. 40.

28. J.J. Fischer, J.J. deBarbadillo, and M.J. Shaw, *Structural Implications of Mechanical Alloying*, eds. F.H. Froes and J.J. deBarbadillo (Materials Park, OH: ASM, 1990), pp. 79-87.

29. R.C. Benn, L.R. Curwick, and G.A.J. Hack, *Potter Metall.*, 11 (1981), pp. 191-195.

30. C.C. Koch, "Processing of Metals and Alloys," *Materials Science and Technology—A Comprehensive Treatment*, ed. R.W. Cahn (Weinheim, Germany: VCH, 1991), p. 193.

31. R. Sundareson and F.H. Froes, *Key Engng. Mater.*, 199 (1989), pp. 29-31.

32. F.H. Froes et al., *Third Int'l. Conf. on High Temperature Intermetallics*, eds. D.P. Pope, S.H. Whang, and C.T. Liu (Warrendale, PA: TMS, 1994), p. 612.

33. D.K. Mukhopadhyay, C. Suryanarayana, and F.H. Froes, *Met. & Mat. Trans. A*, 26A (1995), p. 1939.

34. J. Ding, T. Tsuzuki, and P.G. McCormick, *Nanostruct. Mater.*, 8 (1997), p. 75.

35. F.H. Froes and R.G. Rowe, *Sixth World Conf. on Titanium*, eds. P. Lacombe, R. Tricot, and G. Beranger (Les Ulis Cedex, France: Les Editions de Physique, 1989), p. 655.

36. R. Sundareson, A.G. Jackson and F.H. Froes, in Ref. 35, p. 855.

37. R. Sundareson, A.G. Jackson and F.H. Froes, in Ref. 35, p. 254.

38. F.H. Froes and C. Suryanarayana, *JOM*, 41(6) (1989), p. 12.

39. J. Ding et al., *Appl. Phys. Lett.*, 67 (1995), p. 3804.

40. J. Ding et al., *J. Alloys & Comp.*, 234 (1996), p. L1.

41. J. Ding et al., *J. Phys. D: Solid State Phys.*, 29 (1996), p. 2365.

42. J. Ding, T. Tsuzuki, and P.G. McCormick, *J. Am. Ceram. Soc.*, 79 (1996), p. 2956.

43. T. Tsuzuki, J. Ding and P.G. McCormick, *Physica B*, 239 (1997), p. 378.

44. T. Tsuzuki and P.G. McCormick, *Appl. Physics A*, 65 (1997), p. 607.

45. J. Ding, T. Tsuzuki, and P.G. McCormick, to be published.

46. L. Schultz, K. Schnitzke, and J. Wecker, *J. Appl. Phys.*, 63 (1987), p. 3583.

47. J. Wecker, M. Katter, and L. Schultz, *J. Appl. Phys.*, 69 (1991), p. 6058.

48. J. Wecker et al., *J. Appl. Phys.*, 76 (1994), p. 6238.

49. H. Yang and P.G. McCormick, *J. Matl. Sci.*, 28 (1993), p. 5663.

50. Y. Liu et al., *Proc. 3rd International Conference on Advanced Materials*, (Pittsburgh, PA: MRS, 1993).

51. J. Ding, P.G. McCormick, and R. Street, *J. Alloys Comp.*, 191 (1993), p. 197.

52. J. Ding, P.G. McCormick, and R. Street, *J. Alloys Comp.*, 189 (1992), p. 83.

53. J. Ding, P.G. McCormick, and R. Street, *J. Magn. Magn. Mater.*, 124 (1993), p. L1.

54. K. Schnitzke et al., *Appl. Phys. Lett.*, 57 (1990), p. 2853.

55. W. Liu et al., *J. Alloys and Comp.*, 215 (1994), p. 257.

56. W. Liu et al., *J. Magn. Magn. Mater.*, 131 (1994), p. 413.

57. C. Kuhr, K. Schnitzke, and L. Schultz, *J. Appl. Phys.*, 73 (1993), p. 6026.

58. C. Kuhr et al., *Appl. Phys. Lett.*, 60 (1992), p. 3316.

59. L. Schultz, K. Schnitzke, and J. Wecker, *Appl. Phys. Lett.*, 56 (1990), p. 868.

60. B. Daniel, *J. Matl. Proc. Tech.*, 54 (1995), p. 60.

61. J. Ding et al., *J. Magn. Magn. Mater.*, 123 (1993), p. L239.

62. J. Ding, P.G. McCormick, and R. Street, *J. Magn. and Magn. Mater.*, 124 (1993), p. 1.

63. J. Ding et al., *J. Appl. Phys.*, 75 (1994), p. 1032.

64. K. O'Donnell, C. Kuhr, and J.M.D. Coey, *J. Appl. Phys.*, 76 (1994), p. 7088.

65. K. O'Donnell, C. Kuhr, and J.M.D. Coey, *Proc. 13th Int. Workshop on Rare Earth Magnets and their Appl.* (Birmingham, U.K.: U. of Birmingham, 1993), p. 851.

66. W. Gong and G.C. Hadjipanayis, *J. Appl. Phys.*, 75 (1994), p. 6649.

67. P.A.I. Smith, P.G. McCormick, and R. Street, *Mat. Sci. Forum*, 179-181 (1995), p. 527.

68. P.G. McCormick et al., *J. Magn. Mat.*, 158 (1996), p. 7.

69. P.A.I. Smith et al., *Scripta Metall. Mater.*, 34 (1996), p. 61.

70. T. Alonso et al., *Scripta Metall. Mater.*, 26 (1992), p. 1931.

71. Z. Fu, H.J. Fehl, and W.L. Johnson, *MRS Symp. Proc.* 186 (Pittsburgh, PA: MRS, 1991), p. 169.

72. P.I. Loeff, H. Bakker, and F.R. de Boer, *New Materials by Mechanical Alloying*, ed. E. Artz and L. Schultz (Frankfurt, Germany: DGM, 1989), p. 119.

73. P.S. Goodwin and C.M. Ward-Close, *Proc. 2nd Int. Conf. on Structural Applications of Mechanical Alloying*, ed. J.J. deBarbadillo, F.H. Froes, and R. Schwarz (Materials Park, OH: ASM, 1993), p. 139.

P.G. McCormick is currently director of the Special Research Center for Advanced Mineral and Materials Processing. F.H. Froes is currently the director of the Institute for Materials and Advanced Processes, University of Idaho.

For more information, contact P.G. McCormick, University of Western Australia, Nedlands, WA 6907 Australia, telephone 61893803122; fax 618938801116; e-mail pgm@mech.uwa.edu.au

visit *JOM* on the
World Wide Web at
www.tms.org/pubs/journals/JOM/jom.html



This symposium is being held to recognize Professor J. Keith Brimacombe's landmark contributions to the field of metallurgical process engineering. Professor Brimacombe was renowned for his impact on the continuous casting of steel, gas injection in metallurgical reactors, mathematical modeling of metallurgical processes, processing of solids in rotary kilns, non-ferrous pyrometallurgy, and microstructural engineering in steel and aluminum. The symposium will feature invited international speakers, including many of Professor Brimacombe's former graduate students, who are now leaders in academia, industry, and research.

In recognition of Professor Brimacombe's leadership as President of the Metallurgical Society of CIM (1985), The Minerals, Metals & Materials Society (1993), and the Iron & Steel Society (1995), this symposium will be co-sponsored by the three societies and organized by the Metallurgical Society of CIM.

Please plan to attend this special event to honor Professor J. Keith Brimacombe and to recognize his legacy to our profession.

For information, contact: I.V. Samarasekera, Chair, The Centre for Metallurgical Process Engineering, The University of British Columbia, Advanced Materials and Process Engineering Laboratory, Room 111-2355 East Mall, Vancouver, B.C. V6T 1Z4, Canada, Telephone: (604) 822-3668 or (604) 822-3667, Fax: (604) 822-2965, E-mail: indira@cmpe.ubc.ca

Organizing Committee:

I.V. Samarasekera, Chair, The University of British Columbia
B.G. Thomas, Co-Chair, University of Illinois at Urbana-Champaign
H. Henein, Co-Chair, University of Alberta

Technical Program Co-Chairs:

G. Irons, McMaster University
A.W. Cramb, Carnegie Mellon University

THE BRIMACOMBE MEMORIAL SYMPOSIUM

September 30–October 4, 2000

Vancouver,

British Columbia, Canada



years
en-
val-
ela-
n at
Val-
een
ns. 2
uire
m.

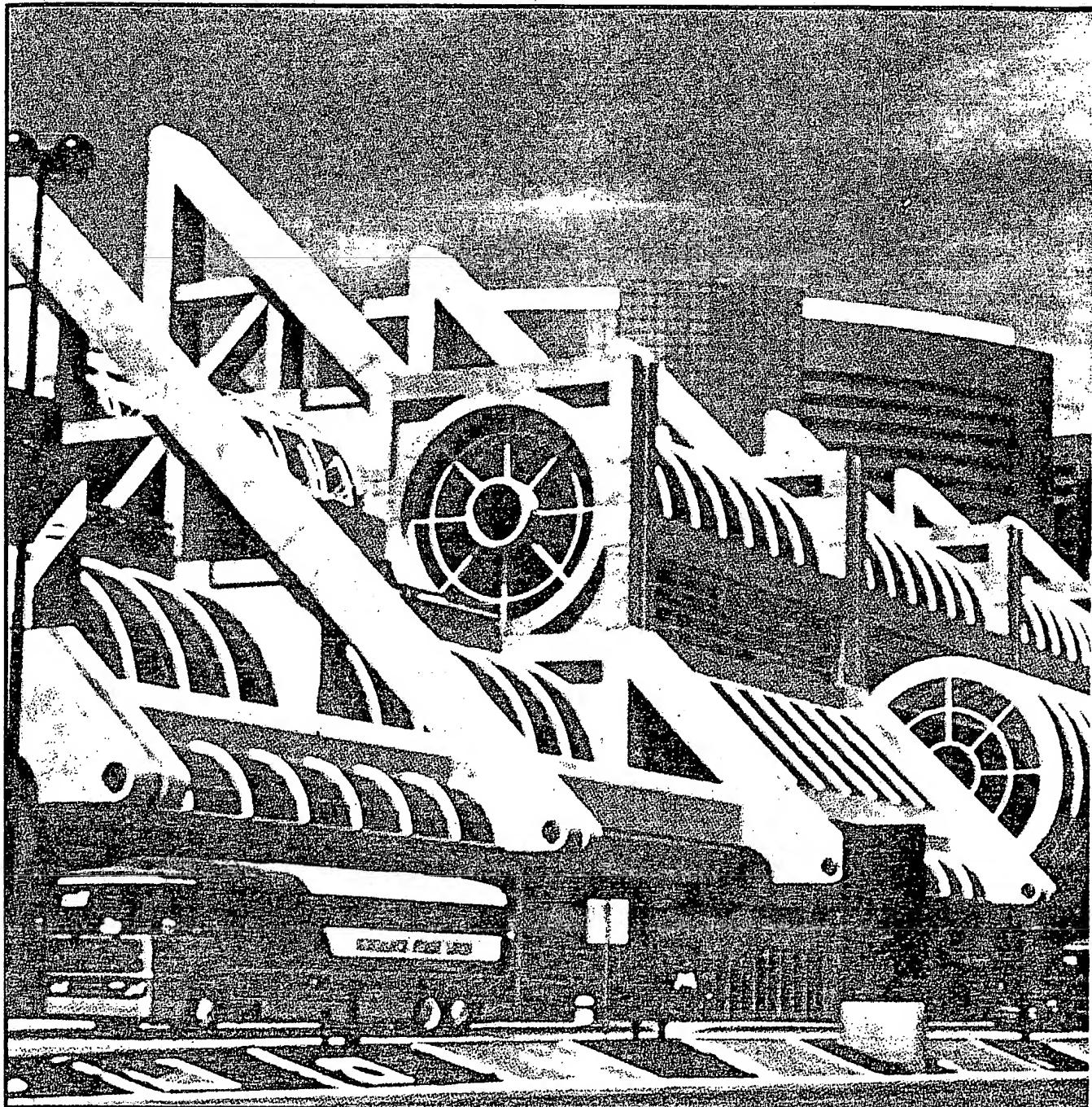
ring
and
; In
tree
ow-
ven
sing
and
icts
3.
ate
own
lud-
ility
eta-
ous
ility
era-
era-
e of
The
cess
tion
ures
han
ow-
ruct-
n of
the
oth-
site
ex-
y of
uch
the
sing
but
1.
ten-
ech-
this
iza-
ral-
ive-

cus-
E.G.
G.B.
i, R.
; T.
also
eler

JOOMI

A publication of The Minerals, Metals & Materials Society

NOVEMBER 1998



*****5-DIGIT 11106
99696 292 183
Case Western Reserve Univ
Elvin Smith Lib
105 Euclid Ave
CLEVELAND OH 44106-1713-55

■ Complete 1999 TMS Annual Meeting &
Exhibition Preview

■ Light Metals: Aluminum and Titanium

Also in this issue

Stainless Steel Apparel—A Long Way from Chain Mail